

SYNTHETIC FUEL PRODUCTION METHOD

[0001] This application is a continuation-in-part of currently pending patent application 10/429,343, filed on May 5, 2003, which was a continuation-in-part of 09/939,229, filed on August 24, 2001, and issued as U.S. Patent 6,558,442 on May 6, 2003, and claims priority under 35 U.S.C. 120 therefrom and also claims priority under 35 U.S.C. 119 from provisional application number 60/228,976, filed August 30, 2000.

BACKGROUND INFORMATION

FIELD OF THE INVENTION

[0002] This invention relates generally to the production of non-traditional fuels, often referred to as synthetic fuels. More particularly, this invention relates to the creation of such fuels using existing stockpiles of coal fines, coal dust, and other similar small particles of virgin coal. More particularly yet, this invention relates to using emulsions of tall oil and tall oil pitch, a by-product of the paper industry, in the creation of such fuels.

DESCRIPTION OF THE PRIOR ART

[0003] For centuries coal has been mined as a source of fuel. During these years, numerous improvements have been made to increase mining efficiency and safety, and to improve the overall quality and purity of the end product. However, one drawback of coal mining is the by-product of coal fines that frequently end up abandoned into waste pits scattered throughout the countryside. These coal fines constitute up to 20% of the coal being mined, and are found in the waste stream generated by the initial washing and filtering of the coal from the mine. Although coal fines include particles as small as dust motes, the term can also include pieces of coal up to about one-half inch in

diameter. This material has traditionally been abandoned to waste, deposited in the form of "coal tips," because it has been economically inefficient to handle such sizes as they are brought to the point of being burned for their energy content. As a result, literally millions of tons of such material has been produced over the years, and currently lays dormant at or near mining sites. Not only does this non-use pose a great waste of valuable natural fuel resources, but it also poses a threat to the surrounding environment. In addition to respiratory hazards presented by the dust-sized particles, the large surface area associated with stockpiles of such particles poses a high risk for spontaneous combustion such as the type known as a dust explosion.

[0004] These environmental issues, together with the growing concern of the limited existing amount of natural fuel resources, has led to an increased interest in utilizing these dormant coal fines, as well as developing an alternative use of virgin coal.

[0005] Attempts to utilize coals fines as fuel include the method disclosed in **White (U.S. Patent No. 5,916,826; issued 1999)**, which teaches a method of pelletizing and briquetting coal fines using bio-binders produced by liquefaction of biomass. Unfortunately, this process is extremely costly, primarily because of the required liquefaction process, which is carried out in an oxygen-free environment at elevated temperatures, e.g. between 450 degrees and 700 degrees F, and elevated pressures, typically between 200 psi and 3,000 psi. The resulting liquid is then sprayed on coal fines that have themselves been heated to at least 250 degrees F., after which the coal and the liquid are allowed to react at about 300-400 degrees F. Although this method serves to alleviate certain environmental concerns, the high costs of reclaiming coal using this process undercuts the basic usefulness of the invention itself.

[0006] Another recent example of the attempt to use coal fines as fuel, **Ford (U.S. Patent No. 5,453,103; issued 1995)**, discloses a method of forming solid fuel pieces from coal fines by combining and mixing water, hydrochloric acid, a conditioner, and a polyvinyl acetate (PVA) emulsion and then compressing the resulting slurry into solid

fuel pieces. Although this process is effective, its requirement of PVA, which must be separately created for this particular use, makes the **Ford** process economically and environmentally inefficient in comparison with a process founded entirely on the use of constituents that are already present, and which some of the constituents are not being devoted to any economical purpose. In other words, a process that consumed both coal fine waste and another hitherto waste element would be more desirable than the **Ford** process.

[0007] A process that does use as input primarily waste products from other industrial operations is revealed by **Major (U.S. Patent No. 6, 013,116; issued 2000)**, which teaches a composition for binding coal fines into larger pieces, typically called briquets. The briquet-binder composition of **Major** can be produced using an asphalt base, sodium carbonate pulping liquor, and a surfactant. However, for optimal binding results, strength-increasing additives such as latex, vinyl derivatives, cellulose, cellulose derivatives, peat moss, starch, starch derivatives, and various pulps need to be added to the binder composition. (The addition of lignosulfate, cement, rubber, and plastics is also taught by **Major**.) Although this process does use various waste products of other industries in transforming coal fines into a more usable fuel source, the complexity of the binding material makes the process quite complex, thereby reducing the economic viability of the overall method.

[0008] An older process of reclaiming coal fines is disclosed in **Dondelewski (U.S. Patent No. 4,357,145; issued 1982)**. In **Dondelewski**, coal fines are combined with a liquid by-product of the pulp and paper industry, namely a liquid containing tall oil, tall oil pitch, or mixtures thereof ("tall oil mix"). Tall oil and tall oil pitch are by-products from the digestion of wood by the Kraft (sulfate) paper manufacturing process. In the **Dondelewski** method, the coal fines are first put into the form of a slurry by mixing them with water. After the slurry has been formed, it is fed to a conditioning tank where it is mixed with tall oil mix. In the conditioning tank, the tall oil mix adheres to and thus coats

the surfaces of the individual coal particles, after which the slurry of now-coated coal particles and excess tall oil mix is introduced into a flotation cell, where the coated coal particles are separated from the excess tall oil mix and most of the water. Vacuum filters, vibratory screens and centrifuges may be used to remove excess liquid, a necessary step since most coal-consuming furnaces cannot tolerate a high moisture content. Again, the process of **Dondelowski** has as its feed stock predominantly industrial by-products, it is very process intensive, first requiring large vats to mix the coal slurry and tall oil mix, then further processing to remove excess water and tall oil mix followed by drying the end product. Thus, the method of **Dondelowski** does not satisfy the condition of using industrial by-products to produce a synthetic fuel that is economically competitive with the fuels that the synthetic fuel is intended to supplant, or which in general is in competition with it as a fuel source.

[0009] Therefore, what is needed is an economical and environmentally friendly method of using industrial by-products traditionally discarded as waste as the feed stock for a new fuel. What is more specifically needed, in view of the millions of tons of coal fines deposited throughout the landscape, is such a method that uses coals fines as all or part of the feed stock. Finally, what is needed is such a process that by whatever means results in a fuel that is economically viable in the marketplace, so that industries now holding hegemony over the referenced industrial by-products, and in particular the coal fines, will be induced to use up those by-products, removing them from the category of stored and hazardous waste.

BRIEF SUMMARY OF THE INVENTION

[0010] It is an object of the present invention to use fines of bituminous coal and other industrial by-products in the creation of a commercially viable fuel. Another object of the present invention is to use such hitherto waste products in a process that is environmentally friendly. A further object of the invention is to provide such a process

that will reduce the overall cost of production, so as to provide industry the economic incentives to make use of the coal fines.

[0011] The term "tall oil mix" as used hereinafter shall refer to tall oil, tall oil pitch, or any combination thereof. This tall oil mix may be modified to the extent that fatty acids, rosin acids, sterols and other constituents may be added or subtracted. The term "coal fines" as used hereinafter is a collective designation for coal particles of bituminous coal, including steam or metallurgical coal fines, coal dust, and all other coal particles that can be used as feedstock for alternative fuels, as well as for bituminous steam or metallurgical coal fines, coal dust, and all other coal particles that could be used directly as a traditional fuel source, but for the fact that they are too small to be able to reach their full economic potential given the present technology. The term "tall oil emulsion" shall refer to any tall-oil-mix, suspension or solution, in water, with or without enhancers.

[0012] The method of the present invention meets the invention's objectives by combining the solids of tall oil mix with coal fines, and more particularly with all or essentially all of the individual particles constituting the coal fines being processed. More particularly, the method of the present invention involves spraying tall oil emulsion into a stream of coal fines, typically an air stream of coal fines formed by letting the coal fines fall under gravity past a spray of tall oil emulsion directed substantially at right angles to the stream.

[0013] As mentioned earlier, tall oil and tall oil pitch are by-products of the digestion of wood by the Kraft (sulfate) paper manufacturing process. Tall oil is 100% organic, non-toxic and non-hazardous to handle. Based on tests carried out on behalf of the inventor, it appears that tall oil reacts chemically with the coal fines after the two components have been brought together according to the method of the present invention. The fuel produced by the present invention is a synthetic fuel in the sense of a synthetic fuel being a fuel "which does not exist in nature... [but rather] is synthesized or manufactured from varieties of fossil fuels which cannot be used conveniently in their

original form." [McGraw-Hill Encyclopedia of Science and Technology, McGraw-Hill, Inc., 1982.] Moreover, it is a synthetic fuel produced by a method resulting in a significant chemical change, based upon the infra-red absorption spectra of the fuel in comparison with the infra-red absorption spectra of the fuel's constituents prior to processing.

[0014] Additionally, when tall oil is combined with coal fines it will contribute in excess of 50,000 Btu's per gallon applied, based upon a 40% solids content tall oil emulsion. It is to be emphasized here that unlike prior-art uses of tall oil, the present method is not aimed at simply producing agglomerations of the basic coal particles. Rather, it is used to produce fuel that continues to exist in small particulate form, but with the tall-oil-mix solids combined with the particulate. In carrying out this method, tall oil emulsion has numerous process advantages over the prior art methods. It can be directly sprayed into passing or free falling coal fines, therefore eliminating the necessity of having large mixing vats to coat the coal fines. Additionally, directly applying tall oil emulsion into the coal fines eliminates the need to separate the coal fines from the tall oil mixing slurry, as taught in the prior art. Elimination of these cost intensive process steps makes the processing of coal fines into a usable fuel a more economical option, and therefore provides an incentive to industry to use this fuel source. A further benefit of using tall oil emulsion is that, in contrast with the relevant prior art described above, it may be applied to the coal fines at a specific rate and specific concentration, without requiring removal of excess material with centrifuges and/or dryers. For example, the tall oil emulsion may be adjusted to contain the desired amount of tall oil to be applied to the coal fines, thus eliminating waste of valuable tall oil resources. The emulsion may be simply sprayed through various nozzles into the coal fines, either in free fall or on conveyor belts. Once sprayed, the treated coal fines need no or little drying, as the water from the emulsion evaporates as part of the process. The treated coal fines may then be sent to an agitator to further facilitate even distribution of the emulsion throughout the coal fines, and/or continue on to be agglomerated by briquetting or

pelletizing apparatus. Nevertheless, it is the process of combining the coal fines with the tall-oil solids that constitutes the heart of the present invention.

[0015] Tall oil emulsions may be prepared in a variety of methods that are well known in the art. Applicants of the present invention have discovered that certain additives or "enhancers" to the tall-oil mix increase the chemical change or reduce the cost while maintaining chemical change that takes place in the coal and enhance the fuel value of the synthetic fuel according to the present invention. Depending upon the specific enhancer, the enhancer is added to the tall oil pitch before emulsification or added to the tall-oil mix after emulsification. For example, in an "enhanced tall-oil mix," poly vinyl acetate (PVA) and/or ethyl vinyl acetate (EVA) is added in an aqueous form with a solids content of between 40 and 55 percent as an enhancer to a tall-oil mix. Depending upon the specific enhancer, the amount of the enhancer that may be added to the enhanced-tall-oil mix ranges from 1 to 50 percent. The use of PVA and/or EVA enhancer reduces by approximately 30% the application rate of the tall-oil mix to the coal fines over that of an unenhanced tall-oil mix. Other suitable materials that serve as enhancers include urea, glycol, lignosulfonate, vegetable materials, such as beet sugar bottoms, molasses, corn bottoms, brewery bottoms, vegetable tall oil, vegetable oil, vegetable pitch, and/or spent frying oil. Again, one or more of these materials is added to the tall-oil mix to create an enhanced tall-oil mix that reduces the cost of producing the synthetic fuel, either by allowing the use of less expensive materials while maintaining chemical change properties, or increasing the chemical change that takes place in the coal, thereby reducing the rate of application and, thus, reducing overall costs. The term "enhanced tall-oil mix" as used hereinafter, includes a tall-oil mix to which at least one of the above-mentioned enhancers has been added.

[0016] A further development of the method of the present invention includes combining a waste material called tar decanter sludge (TDS), a by-product of the steel industry, with the enhanced tall-oil mix, a caustic solution, and water to produce an

enhanced-TDS-tall-oil mix that is then applied as the chemical change agent to bituminous coal fines, to produce a synthetic fuel. Although not necessary to obtain the desired chemical change, light cycle oil (LCO) is preferably also added to the TDS as a thinner, because it improves the mixing process. Before the enhanced-TDS-tall-oil mix is applied to the bituminous coal fines, in facilities where mechanical mixing devices are not available, the components are mixed in batches and combined with one another via pipe systems in a dynamic manner and a homogeneous mix is accomplished via recirculation and a grinding pump. A particularly useful application of this method is to apply the enhanced-TDS-tall-oil mix to bituminous metallurgical coal fines to produce a synthetic fuel.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] The present invention is described with reference to the accompanying drawings. In the drawings, like reference numbers indicate identical or functionally similar elements. Additionally, the left-most digit(s) of a reference number identifies the drawing in which the reference number first appears.

[0018] **Fig. 1** is diagrammatic view of the application process in which emulsified tall oil is joined with coal fines.

[0019] **Fig. 2** is a graphical Fourier Transform Infrared (FTIR) analysis, comparing a solid synthetic fuel consisting of coal fines treated with a 40% solids tall oil emulsion at 0.5% by weight of coal versus the starting materials.

[0020] **Fig. 3** is a graphical Fourier Transform Infrared (FTIR) analysis, comparing a solid synthetic fuel consisting of coal fines treated with a 40% solids tall oil emulsion at 0.75% by weight of coal versus the starting materials.

[0021] Fig. 4 is a graphical Fourier Transform Infrared (FTIR) analysis, comparing a solid synthetic fuel consisting of coal fines treated with a 40% solids tall oil emulsion at 1.0% by weight of coal versus the starting materials.

[0022] Fig. 5 is a graphical Fourier Transform Infrared (FTIR) analysis, comparing a solid synthetic fuel consisting of coal fines treated with a 40% solids tall oil emulsion at 1.25% by weight of coal versus the starting materials.

[0023] Fig. 6 is a graphical Fourier Transform Infrared (FTIR) analysis, comparing a solid synthetic fuel consisting of coal fines treated with a 40% solids tall oil emulsion at 1.5% by weight of coal versus the starting materials.

[0024] Fig. 7 is a schematic illustration of a system for preparing an enhanced-tall-oil mix to apply to coal fines in order to produce the synthetic fuel according to the method of the invention.

[0025] Fig. 8 is a schematic illustration of a system for preparing an enhanced-TDS-tall-oil mix or a non-enhanced-TDS-tall-oil mix to apply to coal fines to produce the synthetic fuel according to the method of the invention.

[0026] Fig. 9 is a graphical Fourier Transform Infrared (FTIR) analysis, illustrating chemical change in synthetic fuel according to the invention relative to initial feedstock, the synthetic fuel comprising coal fines treated with an enhanced-TDS-tall-oil mix at 0.75% by weight of the coal.

[0027] Fig. 10 is a graphical Fourier Transform Infrared (FTIR) analysis, illustrating chemical change in synthetic fuel according to the invention relative to initial feedstock, the synthetic fuel comprising coal fines treated with an enhanced-TDS-tall-oil mix at 1.0% by weight of the coal.

[0028] Fig. 11 is a graphical Fourier Transform Infrared (FTIR) analysis, illustrating chemical change in synthetic fuel according to the invention relative to initial feedstock, the synthetic fuel comprising coal fines treated with an enhanced-TDS-tall-oil mix at 1.25% by weight of the coal.

[0029] Fig. 12 is a graphical Fourier Transform Infrared (FTIR) analysis showing the chemical signature curves of samples of raw coal fines and of the enhanced-tall-oil-mix that are representative of samples used to produce a synthetic fuel comprising 99% coal fines and 1.0% enhanced-tall-oil-mix.

[0030] Fig. 13 is a graphical Fourier Transform Infrared (FTIR) analysis showing the chemical signature curves of samples of raw coal fines and of the enhanced-tall-oil-mix that are representative of samples used to produce a synthetic fuel comprising 99.15% coal fines and 0.85% enhanced-tall-oil-mix.

[0031] Fig. 14 is a graphical Fourier Transform Infrared (FTIR) analysis showing the chemical signature curves of samples of raw coal fines and of the enhanced-tall-oil-mix that are representative of samples used to produce a synthetic fuel comprising 99.25% coal fines and 0.75% enhanced-tall-oil-mix.

[0032] Fig. 15 is a graphical Fourier Transform Infrared (FTIR) analysis showing the chemical signature curves of a synthetic fuel product produced comprising 99.0% coal fines and 1.0% enhanced-tall-oil-mix.

[0033] Fig. 16 is a graphical Fourier Transform Infrared (FTIR) analysis showing the chemical signature curves of a synthetic fuel product produced comprising 99.15% coal fines and 0.85% enhanced-tall-oil-mix.

[0034] Fig. 17 is a graphical Fourier Transform Infrared (FTIR) analysis showing the chemical signature curves of a synthetic fuel product produced comprising 99.25% coal fines and 0.75% enhanced-tall-oil-mix.

[0035] Fig. 18 is a comparison of three different synthetic fuel products of the present invention compared to a conventional synthetic fuel product.

DETAILED DESCRIPTION OF THE INVENTION

[0036] The preferred embodiment of the invention is a method of creating a tall-oil-based emulsion **20** for spraying coal fines to effect a chemical change in the coal and to produce a synthetic fuel. Although the following description illustrates a batch system of production, an automated system can, of course, also be employed. Tall oil is heated to approximately 185 degrees F and piped into a mixing mill. At the same time, water containing the emulsifying agent is piped into the mill. In the Preferred Embodiment, the emulsifying agent is a nonylphenol ethoxylate surfactant with 70 moles of ethoxilation proportioned at 1% by weight of final emulsion, based upon a 100% active form of surfactant and adjusted accordingly for aqueous forms that maybe less than 100% active. For example, a 70% active form of the surfactant will require a 1.43% addition rate. The water and the emulsifying agent are heated to approximately 70 degrees F before entering the mixing mill. The rate at which the pitch and the surfactant and water solution are combined determines the final solids content of the emulsion, which, in the case of the Preferred Embodiment, is 40%. The mixing mill applies a shear motion on the tall oil, breaking the oil into small globules which then become suspended in the water solution. The surfactant aids the emulsification process and serves to keep the tall oil globules from coalescing with one another. The greater the shear applied, the smaller the tall oil globules formed. In general, the smaller the globules, the more stable and homogeneous is the finished tall oil emulsion. The weight of the finished tall oil emulsion **20** at 40% solids content is approximately 8.32 lbs. per gallon.

[0037] As is illustrated in Fig. 1, the tall oil emulsion **20** is nozzle-sprayed into free-falling coal fines **22** from a number of angles and sides so as to promote maximal contact with the coal fines **22**. In the Preferred Embodiment, the coal fines **22** are

sprayed in free fall from a conveyor **16** into a hopper **30**. As shown in **FIG. 1**, a first spray nozzle **23** and a second spray nozzle **24** are located at a first angle and a second angle, respectively, with respect to the free-falling coal fines **22**. This results in emulsion-treated coal fines **25**, which are then introduced into a pug mill (not shown) to further facilitate even distribution of the emulsion throughout the coal fines **25**. Thereafter, the emulsion-treated coal fines **25** (solid synthetic fuel) are conveyed to a stack-out pile (not shown), or may be agglomerated, such as pelletizing or briquetting (not shown). The use of dryers (not shown) may also be used to facilitate the evaporation of the water off the emulsion-treated coal fines **25**. It is, however, a desired feature of this method to minimize the need for drying and removal of excess water by emulsifying the tall oil in advance of application. This facilitates accurate control of the amount of tall oil solids and water (tall oil emulsion **20**) applied.

[0038] **Fig. 2** through **Fig. 6** show data taken from Fourier Transform Infrared (FTIR) analyses of samples containing varying degrees of tall oil emulsion combined with coal fines (referred to as the "product"), compared to analyses of samples of the tall oil emulsion and coal fines taken separately (referred to as "simple mixture"). The data suggest that, when coal fines are brought together with tall oil mix according to the method of the present invention, a chemical reaction takes place between the coal fines and the tall oil that results in synthetic fuel. These figures reflect amounts of tall oil emulsion (at 40% solids) added from 0.5% to 1.5% by weight of coal, as seen in **Tables 1 - 5** shown below. The non-destructive FTIR analyses are able to explore coal's functional group content of the coal. "Functional group" refers to chemical species bonded to aromatic carbon ring structure sites where chemical reactions commonly take place. This analytical technique identifies molecular vibrations due to the absorption of infrared radiation by functional groups with characteristic absorption bands. Such testing is able to ascertain the presence of significant chemical changes in a sample of the coal fines treated with the tall-oil emulsion, in comparison with un-treated coal fines.

Comparison of FTIR Results for Parent Feed and Fuel Product, 0.5% binder				
Absorption peak wave number in cm^{-1}	Possible peak identification	Peak area for parent feed	Peak area for fuel product	Percent change
3386	hydroxyl groups	45.5800	41.9962	9
3037	aromatic CH	3.1771	3.0112	6
2916	aliphatic CH	41.1173	39.8782	3
1596	aromatic ring enhanced by OH bonded C=O group	64.4261	62.2182	4
1439	aliphatic CH_2 and CH_3	25.8677	24.1699	7
1373	cyclic CH_2	0.8716	0.9178	5
1258	C-O and C-O-C	0.9876	0.9981	1
1174	C-O and C-O-C	5.2676	6.6218	26
1102	ethers, esters	1.1618	0.0000	removed
1032	C-O and Si-O	33.5047	21.7171	54
918	alkenes, aldehydes	0.9291	0.0000	removed
858	polycyclic aromatic skeletal structure	1.9846	2.6313	33
806		4.7183	4.2177	12
749		2.5517	3.2966	29
698	aromatic substitution	1.8247	1.0264	78
535	carboxyl groups, thiophenes, heterocyclics	16.8305	13.7271	23
469	Branched and cyclo-alkanes and aliphatic ethers	9.6374	5.9012	63
424	carbonyl, ketones	1.1155	0.6342	76
				avg. 27

Table 1

Comparison of FTIR Results for Parent Feed and Fuel Product, 0.75% binder

Absorption peak wave number in cm^{-1}	Possible peak identification	Peak area for parent feed	Peak area for fuel product	Percent change
3386	hydroxyl groups	45.0112	44.5350	1
3043	aromatic CH	3.0967	3.0786	1
2916	aliphatic CH	39.6251	42.5361	7
1596	aromatic ring enhanced by OH bonded C=O group	62.9332	62.3944	1
1436	aliphatic CH_2 and CH_3	25.2640	24.3238	4
1370	cyclic CH_2	0.8522	0.9002	6
1258	C-O and C-O-C	1.0687	0.9906	8
1174	C-O and C-O-C	4.9082	6.1183	25
1111	ethers, esters	1.0283	0.7372	39
1032	C-O and Si-O	33.5262	26.1635	28
918	alkenes, aldehydes	0.6674	0.5090	31
861	polycyclic aromatic skeletal structure	1.9388	2.3177	20
803		4.6127	4.3129	7
749		2.4942	2.8145	13
698	aromatic substitution	1.8536	1.4927	24
535	carboxyl groups, thiophenes, heterocyclics	16.8466	15.4300	9
472	Branched and cyclo-alkanes and aliphatic ethers	9.6514	8.0703	20
427	carbonyl, ketones	1.0842	0.8475	28

ave. 15

Table 2

Comparison of FTIR Results for: Parent Feed and Fuel Product: 1% binder				
Absorption peak wave number in cm^{-1}	Possible peak identification	Peak area for parent feed	Peak area for fuel product	Percent change
3386	hydroxyl groups	45.5033	42.8306	6
3043	aromatic CH	3.0904	2.9870	3
2916	aliphatic CH	40.0238	42.3137	6
1593	aromatic ring enhanced by OH bonded C=O group	62.9355	61.5011	2
1436	aliphatic CH_2 and CH_3	25.2630	25.1519	0
1370	cyclic CH_2	0.8533	0.9634	13
1252	C-O and C-O-C	1.0099	1.0838	7
1168	C-O and C-O-C	5.1077	5.4345	6
1108	ethers, esters	0.9852	0.7538	31
1032	C-O and Si-O	28.6857	23.2038	24
915	alkenes, aldehydes	0.7853	0.4584	71
861	polycyclic aromatic skeletal structure	1.9390	2.2944	18
803		4.6168	4.2883	8
749		2.4959	2.9337	18
698	aromatic substitution	1.5561	1.3995	11
535	carboxyl groups, thiophenes, heterocyclics	14.8296	12.9285	15
469	Branched and cyclo-alkanes and aliphatic ethers	8.2766	6.7904	22
427	carbonyl, ketones	1.0709	0.9498	13
				avc. 15

Table 3

Comparison of FTIR Results for Parent Feed and Fuel Product 1.25% binder

Absorption peak wave number in cm^{-1}	Possible peak identification	Peak area for parent feed	Peak area for fuel product	Percent change
3386	hydroxyl groups	45.9981	46.5494	1
3043	aromatic CH	3.0840	2.8547	8
2916	aliphatic CH	40.0739	42.7524	7
1599	aromatic ring enhanced by OH bonded C=O group	62.5525	61.3507	2
1436	aliphatic CH_2 and CH_3	24.6754	23.8952	3
1373	cyclic CH_2	0.8542	0.9535	12
1252	C-O and C-O-C	1.1119	1.0077	10
1177	C-O and C-O-C	5.0252	5.9054	18
1108	ethers, esters	0.9864	0.7013	41
1032	C-O and Si-O	33.3901	26.2324	27
918	alkenes, aldehydes	0.7939	0.4602	73
858	polycyclic aromatic skeletal structure	1.9394	2.1960	13
800		4.6210	4.2892	8
749		2.4977	2.9254	17
698	aromatic substitution	1.8269	1.4589	25
535	carboxyl groups, thiophenes, heterocyclics	16.8414	15.9147	6
472	Branched and cyclo-alkanes and aliphatic ethers	9.6561	8.0995	19
427	carbonyl, ketones	1.1232	0.9406	19

ave. 17

Table 4

Comparison of FTIR Results for Parent Feed and Fuel Product 1.5% binder				
Absorption peak wave number in cm^{-1}	Possible peak identification	Peak area for parent feed	Peak area for fuel product	Percent change
3380	hydroxyl groups	46.4957	41.3142	13
3043	aromatic CH	3.0773	2.8595	8
2916	aliphatic CH	40.3441	43.5053	8
1596	aromatic ring enhanced by OH bonded C=O group	61.8963	61.6030	0
1436	aliphatic CH_2 and CH_3	24.6763	23.9078	3
1373	cyclic CH_2	0.8551	1.0021	17
1255	C-O and C-O-C	1.0412	0.9865	6
1171	C-O and C-O-C	5.0542	6.4190	27
1108	ethers, esters	1.1682	0.6352	84
1029	C-O and Si-O	33.4953	27.7601	21
918	alkenes, aldehydes	0.8031	0.4636	73
861	polycyclic aromatic skeletal structure	1.9397	2.3452	21
800		4.6251	4.1618	11
749		2.4987	3.0571	22
695	aromatic substitution	1.8145	1.5304	19
535	carboxyl groups, thiophenes, heterocyclics	16.8145	15.9566	5
469	Branched and cyclo-alkanes and aliphatic ethers	9.6717	8.2476	17
424	carbonyl, ketones	1.0785	0.9090	19
				ave. 21

Table 5

[0039] In order to obtain the spectra shown in **Fig. 2** through **Fig. 6**, the samples were imbedded in potassium bromide pellets, and light in the infrared range of $400 - 4000 \text{ cm}^{-1}$ was passed through the pellets. The chemical bonds present determine the absorption spectrum. For example, typically triple bonds and hydrogen stretching are represented by a spectral region of 4000 cm^{-1} to approximately 1800 cm^{-1} . Double bonded structures and aromatic structures have an FTIR range of approximately 1800 cm^{-1} to 1400 cm^{-1} . Single bond structures consisting of various aromatic substitution bonding have an FTIR range from $1000 - 400 \text{ cm}^{-1}$. Supporting Fourier Transform Infrared (FTIR) data from other laboratories not using potassium bromide pellets and preparing samples with other methodology yield similar results.

[0040] Separate scans of the samples were done and the baselines adjusted for accuracy in the context of comparing the base materials and the manufactured fuel product, and the results can be seen in **Fig. 2** through **Fig. 6**. The differences in peak absorption is a strong indication that the coal fines do in fact react with the tall oil emulsion.

[0041] In a further embodiment of the tall-oil mix described above, an enhanced-tall-oil mix **708** is produced by adding an enhancer **704** to the tall-oil mix **702** in a ratio of about approximately 10% enhancer **704** to approximately 90% tall-oil mix **702**. See **Fig. 7**. Suitable enhancers **704** include such substances as poly vinyl acetate (PVA) and/or ethyl vinyl acetate (EVA), urea, glycol, lignosulfonate, vegetable materials, such as beet sugar bottoms, molasses, corn bottoms, brewery bottoms, vegetable tall oil, vegetable oil, vegetable pitch, and/or spent frying oil. One or more of these enhancers **704** may be added in step **706** to the finished tall-oil mix (emulsion) **702**, to the tall-oil or tall-oil pitch before emulsification, or applied simultaneously as with step **710** with the tall-oil emulsion to coal fines **712**. In an enhanced tall-oil mix **708** using vegetable oil or spent frying oil, the oil is combined with tall-oil pitch **702** in a ratio of approximately 1 part vegetable oil or spent frying oil to approximately 3 parts tall-oil pitch **702**. The

enhanced-tall oil-mix **708** is then applied in step **710** to the coal fines **712** to form a synthetic fuel **714**.

[0042]

[0043] A further development of the synthetic fuel according to the method of the present invention includes a synthetic fuel **838** that is produced by forming an enhanced-TDS-tall-oil mix **830** and applying it to coal fines **712**. The enhanced-TDS-tall-oil mix **830** is formed by combining tar decanter sludge (TDS) **818**, a by-product of the steel industry, and, preferably but optionally, light cycle oil (LCO) **820** with a combination-tall-oil-mix **810**. The combination-tall-oil-mix **810** preferably is comprised of the enhanced tall-oil mix **708**, a caustic solution **804**, and water **806**.

[0044] In the preferred embodiment, the synthetic fuel **838** is approximately 0.64% enhanced-TDS-tall-oil mix **830** and approximately 99.36% coal fines **712**, wherein the TDS **818** and LCO **820** comprise approximately 0.29% and the combination-tall-oil mix **810** comprises approximately 0.35%. In this example the 0.35% combination-tall-oil-mix **810** is comprised of approximately 83% of enhanced-tall-oil mix **708** (which is comprised of approximately 55% enhancer **704**, such as PVA, and approximately 28% tall-oil mix **702**), approximately 8% of a 20% caustic solution **804**, and 9% water **806**. The preferred embodiment uses a 20% caustic solution **804**, but this is for convenience only. It is possible to use the process and system of the present invention with a caustic solution **804** having a strength within the range of 5% to 40%. The percentage amount of the caustic solution **804** and water **806** are adjusted by conventional means according to the chosen strength of the caustic solution **804**. It is further known that a 50% caustic solution **804** would be too concentrated and interfere with the production of the enhanced-TDS-tall-oil mix **830** and the non-enhanced-TDS-tall-oil mix. The ratio of tall-oil mix **702** to enhancer **704**, e.g., PVA or EVA emulsion, that forms the enhanced tall-oil mix **708** and provides the desired chemical change in the production of the synthetic fuel **838**, may vary over a very wide range, with an acceptable ratio of tall-oil

mix **702** being at least as low as 15% to a corresponding 85% or greater of enhancer **704**, e.g., PVA or EVA emulsion. Furthermore, the preferred ratio of enhanced-TDS-tall-oil mix **830** is not limited to 0.64%, but is variable within a range of approximately 0.5% to approximately 0.9%. Rates lower than approximately 0.5% may not provide the desired amount of chemical change when applied to the coal fines **712**; rates higher than approximately 0.9% may not be economical. The enhanced-TDS-tall-oil mix **830** is then applied to the coal fines **712** in order to produce the synthetic fuel **838**. As mentioned earlier, it is not necessary to add the LCO **820** to obtain the necessary chemical change to produce the synthetic fuel **838**. It is advantageous to the process to do so, however, because the LCO **820** thins the TDS **818** and aids mixing.

[0045] In addition, although the use of the chemical enhancers **704** is advantageous and is preferred when producing a synthetic fuel **838** with the TDS **818** and LCO **820** additives, it is not necessary to use the enhanced tall-oil mix **708**. Rather, a non-enhanced-tall-oil mix **802**, i.e. a tall-oil mix **702** without added enhancers **704**, is mixed with caustic solution **804** and water **806** to obtain a combination-tall-oil mix **810** that is non enhanced, which is then combined with TDS **818** and LCO **820** to obtain a non-enhanced-TDS-tall-oil mix **832**. The non-enhanced-tall-oil mix **802** comprises tall oil, tall-oil pitch, or any combination thereof, collectively tall oil mix **702**, without the addition of chemical-change enhancers **704**. This non-enhanced-TDS-tall-oil mix **832** is then applied to the coal fines **712** to produce the synthetic fuel **838**.

[0046] Fig. 8 is a schematic illustration, showing the system **800** for mixing by recirculation a combination-tall-oil mix **810** with the TDS **818** and LCO **820** to produce the enhanced-TDS-tall-oil mix **830** of the present invention. The same system **800** is also used to produce the non-enhanced-TDS-tall-oil mix **832**, but for purposes of illustration and simplicity, reference shall be made to the production of the enhanced-TDS-tall-oil mix **830**.

[0047] The system **800** includes a tank **822**, having a tank inlet **816** and a tank outlet **826**, and a recirculating line **814**, having an inlet **812** and an outlet **840**, wherein the recirculating line **814** connects the tank inlet **816** with the tank outlet **826**. As shown, heating means **824**, such as a conventional heating unit, are included within the tank **822** and a conventional grinding pump **828** is installed in the recirculating line **814** after the tank outlet **826**.

[0048] In operation, the TDS **818** and LCO **820** are introduced into the tank **822** via tank inlet **816**. Once in the tank **822**, the TDS **818** and LCO **820** are heated by the heating means **824** until they reach a desired, predefined temperature. In the preferred embodiment, the TDS **818** and LCO **820** are heated until they reach about 123 degrees F. The TDS **818** and LCO **820** may remain in the tank **822** until the desired temperature is reached, or the TDS **818** and LCO **820** may be circulated out the tank **822**, through the recirculation line **814** and grinding pump **828**, and back into the tank **822** until they reach the desired temperature. The preferred embodiment uses the desired temperature of about 123 degrees F for convenience purpose only. It would be readily apparent to one of ordinary skill to use a comparable temperature, such as a temperature within the range of about 100 to about 135 degrees F.

[0049] The combination-tall-oil mix **808**, which is described in greater detail above, is introduced into the recirculating line **814** via the inlet **812** and fed into the tank **822** via tank inlet **816**. In order to facilitate the heating process within the tank **822**, the combination-tall-oil mix **808** is heated prior to its introduction into the tank **822**. For example, the combination-tall-oil mix **808** is preferably heated to approximately 100 degrees F. Thus, when the warmed combination-tall-oil mix **808** is introduced into the tank **822** containing the heated TDS **818** and LCO **820**, the previously heated TDS **818** and LCO **820** are not unduly cooled. The heating of the combination-tall-oil mix **808** is optional, as well as the prior heating of the TDS **818** and LCO **820**.

[0050] Once all components are in the tank **822**, the combination-tall-oil mix **808**, TDS **818**, and LCO **820** are heated and subsequently passed out the tank outlet **826** and through the grinding pump **828**, thereby producing the enhanced-TDS-tall-oil mix **830**. In the preferred embodiment, the enhanced-TDS-tall-oil mix **830** reaches a desired, predefined, minimum temperature prior to exiting the system **800**. Specifically, the enhanced-TDS-tall-oil mix **830** reaches a temperature within the range of approximately 100 to 135 degrees F, with a preferred temperature of approximately 123 degrees F. It may be necessary to recirculate all of the ingredients until this preferred temperature is achieved.

[0051] In one embodiment in which recirculation is not desired or required, step **834**, such as when the enhanced-TDS-tall oil mix **830** has reached the predefined minimum temperature, the enhanced-TDS-tall-oil mix **830** is then discharged from the recirculating line **814** via the outlet **840**, ready to be applied, in step **836**, to the coal fines **712** to produce the synthetic fuel **838**. In a second embodiment in which recirculation is desired or required, such as to enable the enhanced-TDS-tall-oil mix **830** to reach the predefined minimum temperature, step **834**, the enhanced-TDS-tall-oil mix **830** is not discharged from the recirculating line **814**, but rather is transported back into the tank **822** via the tank inlet **816**. In this second embodiment, the enhanced-TDS-tall-oil mix **830** is passed through the tank **822** for further heating. This recirculating of the enhanced-TDS-tall-oil mix **830** through the grinding pump **828** is repeated until the enhanced-TDS-tall-oil mix **830** achieves the desired predefined minimum temperature and/or homogeneous mixture. Once the desired temperature and/or homogeneous mixture is achieved, the enhanced-TDS-tall-oil mix **830** is discharged from the recirculating line **814** via the outlet **840** and applied, step **836**, to the coal fines **712** as described above.

[0052] This is merely an example of a system **800** that is suitable for producing the enhanced-TDS-tall-oil mix **830** or the non-enhanced-TDS tall-oil mix **832** according to

the invention. Furthermore, the system **800** is designed to make separate batches of such enhanced-TDS-tall-oil mix **830** or the non-enhanced-TDS tall-oil mix **832**. The system **800** is described in these terms for convenience purposes only. It would be readily apparent to one of ordinary skill in the relevant art to use a comparable system without departing from the scope of the present invention.

[0053] Figs. **9 – 11** are graphical representations of the results of Fourier Transform Infrared spectroscopy studies (FTIR) of test samples of the synthetic fuel **838**. The enhanced-TDS-tall-oil mix **830** was mixed with coal fines **712** and then compressed to form the finished synthetic fuel product **838**. The samples of coal were of bituminous metallurgical coal. As seen in each of the figures, there are clear differences in the spectra between the raw coal fines **712** and the synthetic fuel **838**, indicating that the final product has a basic chemical composition that is measurably different from that of the initial feedstock.

[0054] FIG. **9** shows the FTIR curves for raw coal fines **712** and a synthetic fuel comprising 99.25% coal fines **712** and 0.75% enhanced-TDS-tall-oil mix **830**. As seen, a synthetic-fuel curve **920** shows clear differences from a coal-fines-curve **910**. The percentage of chemical change documented with these results is 32%. FIG. **10** shows the FTIR curves for a raw coal fines **712** and a synthetic fuel comprising 99.0% coal fines **712** and 1.0% enhanced-TDS-tall-oil mix **830**. A synthetic-fuel curve **1020** shows clear differences from a coal-fines-curve **1010**. The percentage of chemical change documented with these results is 42%. FIG. **11** shows the FTIR curves for raw coal fines **712** and a synthetic fuel **838** comprising 98.75% coal fines **712** and 1.25% enhanced-TDS-tall-oil mix **830**. A synthetic-fuel curve **1120** shows clear differences from a coal-fines-curve **1110**. The percentage of chemical change documented with these results is 45%.

[0055] FIGS. **12 - 17** illustrate the results of Fourier Transform Infrared spectroscopy (FTIR) analysis on raw coal fines **712**, on the enhanced-tall-oil-mix **708** comprising 90%

tall-oil-mix **702** and 10% PVA **704**, and on a synthetic fuel **714** comprising the coal fines **712** and the enhanced-tall-oil-mix **708**. The results indicate the amount of chemical change between the raw coal fines **712** and the synthetic fuel **714**. The analysis was performed on coal samples treated with the enhanced-tall-oil-mix **708** at three different addition rates by weight of coal: 0.75% (Test 1), 0.85% (Test 2), and 1.0% (Test 3). In addition, signature curves of a mathematical weight combination of the chemical signatures of the representative samples of the raw coal fines **712** and the enhanced-tall-oil-mix **708** for the particular by-weight addition rates were also plotted.

[0056] Fig. 12 shows the chemical signature **1201** of a sample of coal fines **712** and the chemical signature **1202** of a representative sample of the enhanced-tall-oil-mix **708**, the samples being representative of the samples used in Test 1. Similarly, Fig 13 shows the chemical signature **1301** of a sample of coal fine **712** and the chemical signature **1302** of the enhanced-tall-oil-mix **708** representative of the samples used in Test 2, and Fig. 14 shows the chemical signatures **1401** and **1402** for the samples of coal fines **712** and the enhanced-tall-oil-mix **708**, respectively, that are representative of the samples used in Test 3.

[0057] Figs. 15 – 17 show the chemical signature curves for the synthetic fuels **714** and the weight combination curves for Test 1, 2, and 3. Fig. 15 shows a signature curve **1501** for a synthetic fuel **714** comprising 99.0% coal fines **712** and 1.0% enhanced-tall-oil-mix **708** and a signature cuve **1502** for the mathematical combination of the chemical signatures of the raw coal fines **712** and the enhanced-tall-oil-mix **708**. A total net change of 29% was observed between the spectra of the synthetic fuel **714** and that of the weight combination spectra in Test 1. Fig. 16 shows a signature curve **1601** for a synthetic fuel comprising 99.15% coal fines **712** and 0.85% enhanced-tall-oil-mix **708** and a signature cuve **1602** for the mathematical combination of the chemical signatures of the raw coal fines **712** and the enhanced-tall-oil-mix **708**. A total net change of 24% was observed between the spectra of the synthetic fuel **714** and that of

the weight combination spectra. **Fig. 17** shows a signature curve **1701** for a synthetic fuel **714** comprising 99.25% coal fines **712** and 0.75% enhanced-tall-oil-mix **708** and a signature curve **1702** for the mathematical combination of the chemical signatures of the raw coal fines **712** and the enhanced-tall-oil-mix **708**. A total net change of 20% was observed between the spectra of the synthetic fuel **714** in Test 3 and that of the weight combination spectra.

[0058] **Fig. 18** shows four FTIR analysis curves **1801 – 1804** of the chemical composition of four different compositions of the synthetic fuel **714** according to the invention, produced by treating bituminous coal fines **712** with various compositions of a tall-oil-mix **702** comprising a 40% solids tall-oil-pitch emulsion. Curve **1801** shows the chemical signature for a synthetic fuel **714** produced by treating the coal fines **712** with an enhanced tall-oil-mix **798** comprising 25% vegetable oil and 75% of the solids of a 40% tall-oil-pitch emulsion; curve **1802** shows the chemical signature for a fuel in which the coal fines **712** are treated with an enhanced tall-oil-mix **708** comprising 25% vegetable-tall-oil pitch and 75% of the solids of a 40% tall-oil-pitch emulsion; curve **1803** shows the chemical change signature for a fuel in which the coal fines **712** are treated with an enhanced tall-oil mix **708** comprising 25% crude tall oil and 75% of the solids of a 40% tall-oil-pitch emulsion; and curve **1804** shows the chemical signature of a synthetic fuel **714** in which the coal fines **712** are treated with just a 40% solids tall-oil-pitch emulsion.

[0059] It further shall be understood that variations in the formulation of the enhanced tall-oil mix **708**, the enhanced-TDS-tall-oil mix **830**, and the non-enhanced-TDS-tall-oil mix **832** may be contemplated by one skilled in the art without limiting the intended scope of the method according to the invention herein disclosed and as defined by the following claims. In addition, the present invention is described using bituminous coal fines for convenience purpose only. It should be understood that the

system and process for making synthetic fuel and synthetic fuel of the present invention also can be made using sub-bituminous coal fines.